

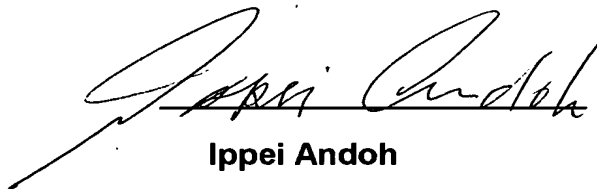
DECLARATION

I, Ippei Andoh, having an address of Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan, hereby declare that I have competent knowledge of the Japanese and English languages, and that I have made the accompanying translation of **United States Patent Application No. 10/816,168** filed on **April 2, 2004**, and that the said translation is true and correct to the best of my knowledge and belief and that this declaration was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

DECLARED by said Ippei Andoh

at Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan

This 6th day of October, 2004



Ippei Andoh

DESCRIPTION

COPPER PLATING BATH AND PLATING METHOD

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to an acid copper plating solution and a plating method. More particularly, the present invention relates to an acid copper plating solution for plating the surface of wafers, which are electronic materials, in particular, for plating wafer surfaces having submicron-level gaps to produce fine copper circuits.

The present invention further relates to a method for plating a substrate to form circuit patterns on semiconductor substrates and the like using a metal plating technique such as a copper plating technique, particularly to a copper plating method for plating wafer surfaces having submicron-level gaps to produce fine copper circuits while ensuring excellent plating film uniformity and filling performance.

The present invention also relates to a plating method capable of depositing copper in fine holes and trenches in electronic circuit substrates such as semiconductor substrates and printed boards which are miniaturized due to increased integration to the extent that it is difficult to form a satisfactory seed layer.

25

Description of Related Art

A copper sulfate plating solution has long been used

as an acid copper plating solution and is used for plating wafers in a recent technology (Japanese Patent Application Laid-open No. 2000-248397).

5 In a wafer processing method, a fine circuit pattern is formed on the wafer surface, followed by copper plating of the wafer surface. The fine circuit pattern formed on this wafer surface has very fine submicron-level gaps, for example.

To uniformly plate copper on a wafer surface having such very fine gaps, the electrocoating conditions must be
10 separately controlled for the area in which copper is plated with comparative ease and the area in which it is difficult to uniformly plate copper by electrocoating, such as the inside of the fine gaps.

Low-k/Cu damascene wiring in logic devices is an
15 important technique for implementing highly integrated/high performance multilayer wiring. Requirements for copper wiring are particularly stringent. In the wake of the era in which a circuit width of 65 nm or less was demanded, more excellent filling performance for fine damascene structures, superior
20 in-plane uniformity for 300 mm wafers, and a further reduction of step difference after plating have been desired. In addition, since barrier metal/seed layers are expected to become markedly thin after the 65 nm generation, satisfying these requirements involves further difficulty.

25 In fact, in conventional cup-type plating apparatuses, the electric resistance of the seed film itself increases due to the decrease in the seed layer thickness. For this reason,

there have been occasions in which in-plane uniformity is impaired due to a decrease in the film thickness from the edge toward the center of the wafers. As a measure for avoiding this phenomenon, a method of controlling the electric field

5 uniformly using an electric field adjuster (a shield plate), a partition anode, and the like is conceivable. This method, however, may require a complicated operation to process a variety of samples when parts and recipes vary according to the types of plating solution and the seed film thickness.

10 Another possible measure is to increase the electric resistance between the anode and cathode (wafer) to the extent that the electric resistance of the seed film itself is no longer predominant over the uniformity of plane.

Based on this idea, a method of increasing the
15 resistance of the plating solution itself by decreasing the sulfuric acid concentration in the plating solution (see USP 6,350,366, for example) and a method of increasing the electric resistance between the electrodes by inserting specific resistors between the electrodes (see M. Tsujimura et al., "A
20 Novel Compact ECD Tool for ULSI Cu Metallization", Proc. ISSM, 2000, pp. 106-109, for example) have been invented and put into practice.

A conventional method for forming a wiring circuit by forming fine trenches and holes in the form of the wiring circuit
25 on an electronic circuit substrate, plating the substrate with copper to fill the trenches and holes with copper, and removing the copper deposited on unnecessary parts has also been a

problem.

Specifically, forming wiring by copper plating using the above method may also cause difficult problems, since the wiring width formed by such fine trenches is anticipated to become as small as 0.1 μm or less in the future due to the increasing wiring density in electronic equipment. One problem is that a thin copper seed layer formed in the fine trenches and holes on the sidewall or bottom may dissolve before the plate film is produced.

Specifically, in a typical method of plating an electronic circuit substrate, a barrier layer is first formed and a copper layer, called a seed layer, functioning as a conductive layer is formed on the barrier layer by sputtering or chemical vapor deposition.

However, even if a copper seed film on the surface of the substrate has a thickness of about 100 nm, the seed film thickness in vias, with a diameter of 0.1 μm (100 nm) and an aspect ratio of about 5, is 10 nm or less due to poor sputter coverage. The seed film thickness in the sidewalls of vias is particularly small.

The present invention has been completed in view of the above situation. Specifically, an object of the present invention is to provide an acid copper plating solution which can be applied to the surface of a wafer or the like having submicron-level gaps to completely fill the gaps with copper plating and, at the same time, form highly uniform copper plating and an electroplating method using the acid copper

plating solution.

Another object of the present invention is to provide a plating method which can provide a thin seed layer with excellent in-plane uniformity and outstanding capability of
5 filling fine damascene structures.

Still another object of the present invention is to provide a plating method capable of producing uniform plating on an extremely thin part of a copper seed film on sidewalls and bottom of vias to produce voidless filling, which has been
10 very difficult to attain using present technologies.

SUMMARY OF THE INVENTION

The present inventors have conducted studies on the components for an acid copper plating solution with an objective
15 of obtaining a copper plating solution which, when applied to the surface of a wafer or the like having submicron-level gaps, can completely fill the gaps with copper plating and, at the same time, can form highly uniform copper plating.

During the course of the study, the inventors have found
20 that, among high molecular weight surfactants (components for controlling electrodeposition reaction) and sulfur-containing saturated organic compounds (components for promoting electrocoating rate) which are contained in common acid copper plating solutions, the high molecular weight surfactants are
25 adsorbed in the area exposed to the plating solution on the surface to be plated having very small gaps and control the electrodeposition reaction in that area. However, in wafers

having submicron-level gaps, such high molecular weight surfactants were found to have a tendency of concentrating the plating current in the edges, particularly, in the edges on the surface side on which extremely minute gaps are formed.

5 The inventors have further found that, to control the electrodeposition reaction in the edges to a great extent, it is desirable to cause a highly hydrophobic and strongly adsorptive high molecular weight surfactant to be adsorbed in the edges and to cause another, less adsorptive and less
10 hydrophobic, high molecular weight surfactant exhibiting relatively small controlling power to be adsorbed in the other areas.

 The inventors also found that if two or more high molecular weight surfactants with different hydrophobicities
15 are used while controlling their concentrations, it is possible to approximate the electrocoating rates in the area in which electrocoating of copper plating occurs comparatively easily and in the area in which electrocoating of copper plating proceeds only unevenly, such as inside the very minute gaps,
20 thereby obtaining uniform plating.

 The inventors have conducted further extensive studies on a plating method which can provide a thin seed layer with excellent in-plane uniformity and an outstanding capability of filling fine damascene structures and, as a result, have found
25 that plating exhibiting both excellent in-plane uniformity and outstanding filling capability can be achieved using a plating bath containing an acid at a concentration above a specific

level and by inserting an electric resistor between the wafer and anode.

The inventors have further studied a method for uniformly producing acid copper plating when the copper seed film is extremely thin and found that if the high molecular weight surfactant is added to an acid copper plating solution at a higher concentration, dissolution of copper in the area in which the copper seed layer is thin, such as the bottom of vias, can be prevented, and voidless filling is possible.

The inventors have further found that an acid copper plating solution containing an organic acid or an inorganic acid at a concentration of 0.4 mol/l is useful to directly plate copper on a substrate of another metal such as Ta, Ti, Al, Ru, Pt, or Ir, without a copper seed film.

Specifically, the present invention provides an acid copper plating solution comprising copper ions, an organic acid or an inorganic acid, chloride ions, high molecular weight surfactant which controls the electrodeposition reaction, and a sulfur-containing saturated organic compound which promotes the electrocoating rate, wherein the high molecular weight surfactant comprises at least two types with different hydrophobicities.

Moreover, the present invention provides an electrolytic plating method characterized by performing plating at a cathode current density in the range of 0.1-30 mA/cm² using any one of the above-mentioned acid copper plating solutions.

The present invention further provides a plating method for forming a plating film on a conductor layer, which is formed on at least a part of a structural object having a concave-convex pattern on a semiconductor substrate, comprising providing a cathode potential to the conductor layer and supplying a plating solution which electrically connects an anode with the conductor layer, wherein the plating solution contains 25-75 g/l of copper ion and 0.4 mol/l or more of an organic acid or inorganic acid and an electric resistor is installed between the conductor layer and the anode.

The present invention further provides a plating method for forming a wiring circuit on an electronic circuit substrate having fine holes and trenches, comprising forming a plating film on a conductor layer, which is formed on at least a part of the substrate, and filling the holes and trenches with copper, wherein the plating film is formed by using an acid copper plating solution containing copper ions, organic or inorganic acid, chloride ions, sulfur-containing saturated organic compound, and high molecular weight surfactant controlling electrocoating at a concentration of 500 ppm or more.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a chart showing the relationship between the porosity and electric conductivity, wherein Type A indicates SiC and Type B indicates Al_2O_3 .

Figure 2 is a chart showing the relationship between the pore size and electric conductivity.

Figure 3 is a drawing schematically showing an embodiment of a first plating method, wherein 1 indicates a plating cell, 2 indicates a wafer, 3 indicates an anode, 4 indicates an electric resistor, 5 indicates a wafer seal, and 6 indicates a cathode.

Figure 4 shows a result of measuring a film thickness distribution along the diameter of a 200 mm wafer, wherein A and B indicate the results respectively when the seed layer is 20 nm or 60 nm.

Figure 5 shows a result of measuring a film thickness distribution along the diameter of a 300 mm wafer, wherein A and B indicate the results respectively when the seed layer is 20 nm or 60 nm.

Figure 6 is a drawing showing the thickness distribution when plating is carried out in different plating thicknesses, wherein A, B, and C respectively indicate the thicknesses of 0.5 μm , 1.0 μm , and 2.5 μm .

Figure 7 is a chart showing the relationship between the sulfuric acid concentration in a usual copper sulfate plating solution and the electric conductivity.

Figure 8 is a drawing showing the calculation result of the electric conductivity and thickness distribution when the seed layer is varied by the finite element method (FEM).

Figure 9 is a drawing schematically showing a chip testing instrument used in Examples, wherein 11 indicates a plating bath, 12 indicates a substrate, 13 indicates an anode, 14 indicates a plating solution, 15 indicates a stirrer, 16

indicates a substrate holder, and 17 indicates an electric source.

Figure 10 is a drawing showing an embodiment of electric current control.

5 Figure 11 is a drawing showing another embodiment of electric current control.

DETAILED DESCRIPTION OF THE INVENTION

10 A first embodiment of the present invention is an acid copper plating solution comprising copper ions, an organic acid or an inorganic acid, chloride ions, high molecular weight surfactant which controls an electrodeposition reaction, and a sulfur-containing saturated organic compound which promotes the electrocoating rate, wherein the high molecular weight
15 surfactant comprises at least two types with different hydrophobicities (this embodiment hereinafter referred to from time to time as "acid copper plating solution").

20 The second embodiment of the present invention is a plating method for forming a plating film on a conductor layer, which is formed on at least a part of a structural object having a concave-convex pattern on a semiconductor substrate, comprising providing a cathode potential to the conductor layer and supplying a plating solution which electrically connects an anode with the conductor layer, wherein the plating solution
25 contains 25-75 g/l of copper ion and 0.4 mol/l or more of an organic acid or inorganic acid and an electric resistor is installed between the conductor layer and the anode (this

embodiment hereinafter referred to from time to time as "first plating method"). The third embodiment of the present invention is a plating method for forming a wiring circuit on an electronic circuit substrate having fine holes and trenches, comprising
5 forming a plating film on a conductor layer, which is formed on at least a part of the substrate, and filling the holes and trenches with copper, wherein the plating film is formed by using an acid copper plating solution containing a copper ion source, organic or inorganic acid, chloride ions,
10 sulfur-containing saturated organic compound, and high molecular weight surfactant controlling electrocoating at a concentration of 500 ppm or more (this embodiment hereinafter referred to from time to time as "second plating method"). These embodiments will now be described.

15 The acid copper plating solution of the first embodiment comprises copper ions, an organic acid or an inorganic acid, and chloride ions as essential components. An example of the inorganic acid in the acid copper plating solution is sulfuric acid and examples of the organic acid include alkane sulfonic
20 acids such as methansulfonic acid, and pyrophosphoric acid.

In addition, at least a high molecular weight surfactant, which inhibits the electrodeposition reaction, and sulfur-containing saturated organic compound, which promotes the electrocoating rate, are added to and used in the acid copper
25 plating of the present invention.

As the high molecular weight surfactant, compounds consisting of a hydrophilic moiety (group) and a hydrophobic

moiety (group) can be given, for example. As examples of the hydrophilic moiety of the high molecular weight surfactant, a polyhydric alcohol residue, polyethylene glycol residue, amine group, quaternary ammonium group, pyridinium group, sulfonium group, phosphonium group, polyethylene polyamine group, carboxyl group, sulfonic acid group, sulfate group, phosphate group, phosphonic acid group, amino acid residue, betaine, amino sulfate group, and sulfobetaine can be given. As examples of the hydrophobic moiety, moieties of a triglyceride, fatty acid, fatty alcohol, resin acid, n-paraffin, naphthenic acid, α -olefin, alkyl benzene, alkyl phenol, polyoxyalkylene glycol, completely fluorinated fatty acid and fatty alcohol, partially fluorinated fatty acid and fatty alcohol, polysiloxane, and the like can be given. Of the above hydrophilic moieties, the polyhydric-alcohol residue is preferably selected from the group consisting of a glycerol residue, glucose residue, sucrose residue, and amino alcohol residue.

As more specific examples of the high molecular weight surfactant, a fatty acid salt, rosin acid salt, alkyl polyoxyethylene sulfate, α -olefin sulfonate, alkyl naphthalene sulfonate, lignin sulfonate, alkyl phosphate, primary amine salt, alkyl trimethyl ammonium salt, alkyl polyoxyethylene amine, N-alkyl β -aminopropionic acid, N-alkyl sulfobetaine, N-alkylhydroxyl sulfobetaine, lecithin, silkyl polyoxyethylene ether, fatty acid polyoxyethylene ester, fatty acid sorbitan ester, fatty acid sucrose ester, 1,3-dioxalane polymer, polypropylene glycol, polypropylene propanol,

polyethylene glycol, polyethylene glycol derivative, oxylalkylene polymer, copolymer of ethylene oxide and propylene oxide, and fatty acid polyglycerol ester can be given.

In the acid plating solution of the present invention,
5 two or more high molecular weight surfactants with different hydrophobicities must be selected and used. There are two cases for the selection. In one case, the two or more high molecular weight surfactants are nonionic surfactants. In the other case, among the two or more high molecular weight surfactants, one
10 or more are nonionic surfactants, and one or more are different surfactants, i.e. an anionic surfactant, cationic surfactant, or amphoteric surfactant.

When two or more high molecular weight surfactants are nonionic surfactants, a nonionic surfactant with comparatively
15 strong hydrophobicity must be used at a concentration lower than the concentration of a nonionic surfactant with comparatively weak hydrophobicity. The reason is that although it is desirable to use a strongly adsorptive nonionic surfactant with strong hydrophobicity for the edge parts to significantly
20 control the electrodeposition reaction and to use a less hydrophobic nonionic surfactant with a smaller controlling effect for the other parts to cause copper to deposit, the nonionic surfactant with strong hydrophobicity must be used at a concentration lower than the concentration of the nonionic
25 surfactant with weak hydrophobicity because the total area of the edge parts is smaller than the total area of other parts.

Although there are no specific limitations to the

concentration of these nonionic surfactants, the concentration of the nonionic surfactant with strong hydrophobicity is preferably not more than the critical micelle concentration in an acid copper plating solution, and the concentration of the nonionic surfactant with weak hydrophobicity is preferably not less than the critical micelle concentration in the acid copper plating solution. In particular, it is preferable that both the concentration of the nonionic surfactant with strong hydrophobicity is not more than the critical micelle concentration in an acid copper plating solution, and the concentration of the nonionic surfactant with weak hydrophobicity is not less than the critical micelle concentration in the acid copper plating solution. Controlling the concentrations in this manner ensures accurate and fine copper plating inside very small gaps.

A micelle herein refers to an aggregate of molecules or ions which a surfactant at a concentration greater than a certain level forms in a solution and a critical micelle concentration (cmc) indicates the concentration at which such a micelle is formed. Although the critical micelle concentrations of many surfactants in aqueous solutions are known, it is necessary in the present invention to determine the critical micelle concentration in the acid copper plating solution and to control copper plating operations on the basis of such a concentration. To determine the critical micelle concentration, a surfactant is added to an acid plating solution having the same concentration as the acid copper plating

solution to be used to make various concentrations and the concentration at which the physicochemical characteristics greatly change is determined. As examples of the physicochemical characteristics used for detecting the critical micelle concentration, detergency, surface tension, interfacial tension, osmotic pressure, equivalent conductance, and high frequency conductivity can be given.

When one of the two or more high molecular weight surfactants is a nonionic surfactant and one or more are different surfactants (a cationic surfactant, a nonionic surfactant exhibiting cationic properties under highly acidic conditions (e.g. at pH 4 or less), or an amphoteric surfactant), the concentration of the nonionic surfactant must be higher than the concentration of the other surfactants. Specifically, the ionic surfactant other than the nonionic surfactant (e.g, a cationic surfactant, a nonionic surfactant exhibiting cationic properties under highly acidic conditions, and an amphoteric surfactant) is preferably used at a low concentration because these surfactants are preferentially adsorbed in edge parts with a small total area by controlling the current and voltage.

Although there are no specific limitations to the concentrations of the nonionic surfactants and other surfactants, the concentration of the surfactant other than the nonionic surfactant is preferably less than the critical micelle concentration in an acid copper plating solution, and the concentration of the nonionic surfactant is preferably more than the critical micelle concentration in the acid copper

plating solution. In particular, it is preferable that both the concentration of the nonionic surfactant is more than the critical micelle concentration in an acid copper plating solution, and the concentration of the other surfactant is less than the critical micelle concentration in the acid copper plating solution. Controlling the concentrations in this manner ensures accurate and fine copper plating inside very small gaps.

The reasons for causing a surfactant with a small electrodeposition controlling effect (a nonionic surfactant with comparatively low hydrophobicity in the former case and a nonionic surfactant in the latter case) to be adsorbed in very small gaps are to obtain a more precise and fine plating film using the effect of a later-described sulfur-containing organic compound and to control dissolution of the copper seed layer by chlorine, acids, and the like contained in the plating solution.

In the acid copper plating solution of the present invention, a sulfur-containing organic compound is used as an additive in addition to the high molecular weight surfactant. The sulfur-containing organic compound promotes the rate of electrocoating copper onto the plated surface. Since the sulfur-containing organic compound has a molecular weight comparatively smaller than the high molecular weight surfactant, the sulfur-containing organic compound can easily enter very small gaps, thereby promoting the electrocoating rate of copper plating inside the small gaps. The sulfur-containing organic

compound may be added in an amount of 0.1-200 mg/l.

The acid copper plating solution of the present invention may further contain a nitrogen-containing saturated organic compound or an organic dye compound for controlling the leveling of copper plating. Although the effect of these compounds is small at the start of the plating operation, i.e. at an early stage of plating electrocoating, the compounds play a role of providing uniform copper electrocoating irrespective of the plating surface configuration after the copper plating electrocoating has proceeded to some extent. This ensures that the final copper plating is highly leveled. Although one or more types of nitrogen-containing saturated organic compounds or organic dye compounds may be added in an amount of 0.01-20 mg/l, these nitrogen-containing saturated organic compounds or organic dye compounds may not be required according to the high molecular weight surfactant and the sulfur-containing organic compound selected.

Although there are no specific limitations to the concentrations of copper ions, the organic acid or inorganic acid, and chloride ions which are the basic components of the acid copper plating solution of the present invention, preferable concentration ranges for ensuring copper plating with excellent uniformity and filling properties are as follows.

Specifically, when copper sulfate is used as a copper ion source, for example, the amount of the copper sulfate, as pentahydrate, is preferably in the range of 100-240 g/l. If

the concentration of copper sulfate is less than 100 g/l, the amount of copper ions supplied to the plated surface is insufficient, resulting in inadequate filling of very small gaps; if more than 240 g/l, copper precipitate tends to be produced. The concentration of sulfuric acid is preferably 10-100 g/l. If the sulfuric acid concentration is less than 10 g/l, the voltage is high and burnt plating tends to occur; if more than 100 g/l, leveling and filling properties decrease. The concentration of chlorine is preferably 10-90 mg/l. If the chlorine concentration is less than 10 mg/l, uniform electrocoating is impossible; if more than 90 mg/l, copper chloride tends to precipitate.

Copper plating using the acid copper plating solution of the present invention can be carried out under conventional plating conditions without any specific limitations. Specifically, the plating can be carried out at a liquid temperature of about 18-30°C and a cathode current density of 0.1-30 mA/cm².

The concentration of the high molecular weight surfactant in the plating solution must be controlled as mentioned above. The concentration can be controlled according to a known method by appropriately adding the high molecular weight surfactant while monitoring its concentration.

Control by means of the critical micelle concentration can be carried out by preparing a test solution with the same composition as the copper sulfate plating solution to be used.

The critical micelle concentration of this solution is determined to control the operation based on this concentration.

5 The first plating method of the second embodiment of the present invention is a plating method for forming a plating film on a conductor layer, which is formed on at least a part of a structural object having a concave-convex pattern on a semiconductor substrate, comprising providing a cathode potential to the conductor layer and supplying a plating solution which electrically connects the anode to the conductor layer, wherein the plating solution contains 25-75 g/l of copper ion, 0.4 mol/l or more of an organic acid or inorganic acid, and an electric resistor is installed between the conductor layer and the anode.

15 The copper plating solution used in the first plating method contains 25-75 g/l of copper ion and 0.4 mol/l or more of an organic acid or inorganic acid.

As examples of the copper ion source used for the copper plating solution, copper compounds selected from the group consisting of copper sulfate, copper oxide, copper chloride, copper carbonate, copper pyrophosphate, copper alkane sulfonate, copper alkanol sulfonate, and organic acid copper can be given.

As examples of the organic acid or inorganic acid (hereinafter referred to as "acids"), sulfuric acid, alkane sulfonic acid, and alkanol sulfonic acid can be given.

The concentration of these acids is 0.4 mol/l or more.

If the concentration is lower than 0.4 mol/l, the filling properties may be impaired. A preferable concentration of the acids is 0.4-1.0 mol/l.

5 The addition of an organic acid or an inorganic acid at a concentration of 0.4 mol/l or more is preferable to directly plate copper on a substrate of another metal such as Ta, Ti, Al, Ru, Pt, or Ir, without a copper seed film.

10 A particularly preferable combination of the acid and copper ion source used in the first plating method of the present invention is the combination of sulfuric acid and copper sulfate, particularly, a combination in which the copper ion concentration is 58 g/l or less.

15 In the first plating method, an electric resistor must be inserted between the wafer and anode. As the electric resistor, ceramic porous materials such as SiC and Al₂O₃, PTFE filter, and porous plastics such as polyethylene in the form of a sheet can be used.

20 Preferable electric resistors are those capable of reducing the electric conductivity during the plating operation to one half or less of the electric conductivity during a normal plating operation, for example, 3 s/m or less.

25 Other than the above features, conventionally known methods are appropriately employed in the first plating method of the present invention. For example, chloride ions and additives at suitable concentrations can be added to the plating bath. As the additives, high molecular weight surfactants for controlling electrodeposition reaction, sulfur-containing

saturated organic compounds for promoting the electrocoating rate, nitrogen-containing saturated organic compounds for controlling leveling, organic dye compounds, and the like can be used either individually or in combination of two or more.

5 As the anode for plating, commonly known soluble electrodes and insoluble electrodes can be used. Also, the wafers to be plated may be those formed with a barrier layer or a seed layer according to a conventional method. Furthermore, it is possible to use various types of plating apparatuses, such
10 as a face-up type apparatus, face-down type apparatus, and vertical-type apparatus.

 The second plating method of the third embodiment of the present invention is a plating method for forming a wiring circuit on an electronic circuit substrate having fine holes
15 and trenches, comprising forming a plating film on a conductor layer, which is formed on at least a part of the substrate, and filling the holes and trenches with copper, wherein the plating film is formed by using an acid copper plating solution containing copper ions, organic or inorganic acid, chloride
20 ions, sulfur-containing saturated organic compound, and high molecular weight surfactant controlling electrocoating at a concentration of 500 ppm or more.

 The second plating method utilizes the effect of the high molecular weight surfactant used as the additive for
25 controlling electrocoating in an acid copper plating solution to prevent dissolution of copper by an acid and to protect a thin copper seed film from the action of the acid contained in

the acid copper plating solution.

The high molecular weight surfactants used in the second plating method may be those used as the additive for controlling electrocoating , for example, polyethylene glycol with a
5 molecular weight of 1,000-5,000 and polypropylene glycol with a molecular weight of 500-1,000 (such a high molecular weight surfactant is hereinafter referred to as "a polymer component").

The polymer component, however, must be added in an
10 amount far greater than the amount used for conventional acid copper plating solutions. Specifically, the polymer component, which is used in an amount of about 50-300 ppm in conventional acid copper plating solutions, must be used in an amount of 2-20 times that amount, i.e. about 500-1,000 ppm in the second
15 plating method.

Except for using the polymer component in the above concentration, the acid copper plating solution of the second plating method is prepared according to the same composition as the known acid copper plating solutions.

20 For example, copper ions can be supplied from copper compounds such as copper sulfate and copper alkane sulfonate, and sulfuric acid and alkane sulfonic acid can be used as an anion component. Moreover, the acid copper plating solution preferably contains chloride ions. As additives,
25 sulfur-containing saturated organic compounds such as bis(3-sulfopropyl)disulfide (SPS) and mercaptopropane sulfonic acid (MPS) and nitrogen-containing polymers such as

a quaternary salt of polydialkylaminoethyl acrylate, polydiallyldimethylammonium chloride, polyethylene imine, quaternary salt of polyvinyl pyridine, polyvinyl amidine, polyallyl amine, and polyamine sulfonic acid can be used.

5 The amounts of each component for the acid copper plating solution of the second plating method can be appropriately selected. A preferable compositional range for copper sulfate plating, for example, is as follows.

	Preferable range	Particularly preferable range
Copper sulfate pentahydrate	100~250 g/l	180~230 g/l
Sulfuric acid	10~100 g/l	10~60 g/l
Chlorine	50~70 ppm	55~65 ppm
Polymer component	500~1500 ppm	700~1200 ppm
Sulfur-containing organic compound	1~5 ppm	1~3 ppm
Nitrogen-containing polymer	1~100 ppm	1~ 50 ppm

10

To perform the second plating method, a barrier layer and copper seed layer (conductor layer) are first formed on an electronic circuit substrate having fine holes and trenches according to a conventional method and the electronic circuit
15 substrate is then dipped in the acid copper plating solution containing copper ions, an organic or inorganic acid, chloride ions, and the polymer component at a concentration of 500 ppm

or more, whereupon copper is plated.

In plating copper, although it is possible to pass an electric current after the plated material has been entirely dipped, a more preferable method is applying a cathode potential to the seed layer (conductor layer) when the material is dipped. Either a constant voltage or a constant current may be used for applying the cathode potential when dipping. A combination of these and a combination of an additional means such as a pulse current or PR current can also be used.

Next, an example of the electric potential controlling method for plating will now be described. Figure 10 shows a controlling method of plating, consisting of a constant voltage control and a two stage constant current control, using an apparatus (for example, a chip tester shown in Figure 9) having a plating power supply 7, of which the cathode is connected to a substrate 2 secured by a substrate holder 6 to function as a cathode electrode and the anode is connected to an anode electrode 3.

In the example of the control shown in Figure 10, the substrate 2 is put into a plating bath 1 while applying a constant voltage control between the cathode electrode and the anode electrode (t_0-t_1), a low constant current i_1 is applied to gradually grow a plating film (t_1-t_2), then, when the plating film has grown to a certain thickness, a high constant current i_2 ($i_2 > i_1$) is applied to rapidly grow the plating film and fill copper.

Figure 3 shows another example of the control for the

plating, which initially employs a constant voltage control, followed by a constant low current control, a constant current control after reversing the anode and cathode, and finally a constant high current control.

5 In the example of the control shown in Figure 11, after putting the substrate 2 into the plating bath while controlling at a constant voltage, a low constant current i_3 is passed to gradually grow the plating film. Then, the current (voltage) is switched to reverse the cathode electrode into the anode and
10 the anode electrode into the cathode, and a constant current ($-i_4$) is applied (t_5-t_6). After switching the direction of the current (voltage), a high constant current i_2 ($i_2 > i_1$) is applied to rapidly grow the plating film and fill copper. In this manner, the plated film near the openings on the substrate surface in
15 which the plated film becomes thick faster than in the bottoms of the holes and trenches is etched while the holes and trenches are filled, whereby flatness of the resulting plated film can be improved.

 Although the plating may be completed using the acid
20 copper plating solution containing 500 ppm or more of the above polymer component, it is possible to fill the holes and trenches after switching the acid copper plating solution to a conventional acid copper plating solution containing a smaller amount (10-100 ppm) of the polymer component.

25 In this instance, it is preferable to use the acid copper plating solution containing 500 ppm or more of the above polymer component until the plated film thickness on the substrate

surface becomes about 50-200 nm and to plate copper for the plated film thickness from 200 nm to 2,000 nm using a conventional acid copper plating solution containing a smaller amount (10-100 ppm) of the polymer component.

5 Various plating apparatuses, such as a face-up type plating apparatus (impregnation plating apparatus), a face-down type plating apparatus (DMP: damascene metal plating), and a test machine in a chip level, can be used for the second plating method.

10 Plating conditions that can be employed are a current density of 1-50 mA/cm² and a plating solution temperature of 15-30°C, while stirring by means of substrate rotation, jet stream, or air bubbling.

 As a typical example of the substrate on which uniform
15 plating is formed while preventing formation of voids using the above-described second plating method, a semiconductor substrate having holes and/or trenches with vias or an opening width of 1 μm or less, preferably 0.1-0.2 μm, an aspect ratio of 4 or more, preferably 5 or more, and provided with a copper
20 seed film of about 1-100 nm on the surface can be given.

 When significantly controlling the electrodeposition reaction in the edge parts by using a strongly adsorptive surfactant with strong hydrophobicity and controlling deposition of copper on the other parts by using a less
25 hydrophobic surfactant with a smaller controlling effect, the surfactant with strong hydrophobicity is used at a concentration lower than the concentration of the surfactant

with weak hydrophobicity in the acid copper plating solution of the present invention taking into consideration that the total area of the edge parts is smaller than the total area of the other parts.

5 As a result of decreasing the concentration of the surfactant with strong hydrophobicity, deposition is controlled mainly in the edge parts by the acid copper plating solution of the present invention, allowing less hydrophobic surfactants and other additives to invade gaps to form uniform
10 plating, not only on the surface of the wafers but also in the gaps.

 In the first plating method of the present invention, filling properties are promoted by increasing the acid concentration in the plating bath to 0.4 ml/l or more and, at
15 the same time, excellent in-plane uniformity is ensured by inserting an electric resistance between the anode and the wafer.

 The combination of these features has satisfied the two contradictory characteristics of excellent in-plane
20 uniformity and excellent filling of fine circuit trenches and vias.

EXAMPLES

 The present invention will be described in more detail
25 by way of Examples, Comparative Examples, and Reference Examples. However, these examples should not be construed as limiting the present invention.

The critical micelle concentration of the high molecular weight surfactants used in the examples was determined as a value saturating the surface tension of the copper sulfate plating solution of the following composition
5 obtained by measuring the surface tension using a Traube's stalagmometer (the value is hereinafter referred to as "measured cmc").

(Copper sulfate plating solution composition)

10	Copper sulfate (as pentahydrate)	180 g/l
	Sulfuric acid	25 g/l
	Chlorine	60 ppm

Example 1

15 Plating test using a combination of two nonionic surfactants

Polypropylene glycol (PPG) with a molecular weight of about 3,000 (as a nonionic surfactant with high hydrophobicity) and polyethylene glycol (PEG) with a molecular weight of about
20 3,000 (as a nonionic surfactant with low hydrophobicity) were added to the above copper sulfate plating solution in amounts to provide concentrations of 5 mg/l and 20 mg/l, respectively. As another additive, 5 mg/l of bis(3-sulfopropyl)disulfide (SPS) was added.

25 A test piece provided with fine trenches with a width of 180 nm and an aspect ratio of 5, made electrically conductive by a known method, was plated using this copper-sulfate plating

solution under the following conditions.

(Plating conditions)

Plating temperature: 25°C

5 Current density: 10 mA/cm²

Plating time: 1 minute

After plating, the fine trenches were cut and the copper filling conditions were inspected using a microscope to confirm
10 that the copper was completely filled in without any voids.

Although the measured cmc of the PPG used was 20 mg/l and that of the PEG was 20 mg/l, excellent filling of the fine trenches was achieved by using PPG with high hydrophobicity at a comparatively low concentration and PEG with low
15 hydrophobicity at a low concentration.

The reason is presumed to be as follows. PPG used at a low concentration no greater than the measured cmc is preferentially adsorbed near the openings of vias and can be adsorbed only with difficulty to the bottom of the fine trenches,
20 whereas PEG used at a high concentration no lower than the measured cmc can be adsorbed both to the bottom and openings of the fine trenches due to the high concentration. As a result, both the PPG and PEG are adsorbed near the openings of vias to significantly control plating. Therefore, plating from the
25 bottom of trenches without blocking the openings is possible.

It is possible to use a suitable combination of nonionic surfactants with different hydrophilicities and

hydrophobicities selected from the group consisting of natural lauryl alcohol, natural alcohol, natural oleyl alcohol, synthetic primary alcohol, nonylphenol ethoxylate, octylphenol ethoxylate, and special phenol ethoxylate.

5

Example 2

Plating test using a combination of a nonionic surfactant and another surfactant

10 A combination of 20 mg/l of PEG with a molecular weight of about 3,000 (as a nonionic surfactant) and 5 mg/l of polyoxyethylene dimethyl ammonium chloride which is a cationic surfactant (as another surfactant) was added to the above copper sulfate plating solution. As another additive, 5 mg/l of SPS was added.

15 The same plating test as in Example 1 was carried out to examine the copper filling conditions in fine trenches. As a result, excellent copper filling without voids was confirmed.

Although the measured cmc of the PEG used was 20 mg/l and that of the polyoxyethylene dimethyl ammonium chloride was 20 mg/l in this Example, excellent filling of fine holes was achieved by using PEG which is a nonionic surfactant at a comparatively high concentration of more than the measured cmc and polyoxyethylene dimethyl ammonium chloride which is a cationic surfactant at a low concentration below the measured
25 cmc.

The same reason as in Example 1 is presumed for this excellent filling. Specifically, polyoxyethylene dimethyl

ammonium chloride which is a cationic surfactant is preferentially adsorbed near the opening of the fine trenches, but can be adsorbed only with difficulty to the bottom of the vias, whereas PEG is adsorbed both to the bottom and opening of the fine trenches. As a result, both the polyoxyethylene dimethyl ammonium chloride and PEG are adsorbed near the openings of the vias to significantly control plating. Therefore, plating from the bottom of trenches without blocking the openings is possible.

In addition to the above effects, the combination of a nonionic surfactant at a comparatively high concentration and a cationic surfactant at a comparatively low concentration exhibits an effect of producing uniform plating in coarse and dense patterns formed from fine holes and trenches.

Wafers and the like on which fine circuit patterns are formed have an area with densely formed fine circuits and an area with only sparsely formed circuits. The current supplied per unit area is higher in the area in which fine circuits are densely formed, whereas a cationic surfactant with a higher plating control effect is attracted to the area with densely formed fine circuits having a higher current value. As a result, a uniform plating control effect can be obtained as a whole.

As other nonionic surfactants, a mono-long-chain alkyl-type surfactant, di-long-chain alkyl-type surfactant, diamide quaternary cationic surfactant, diester quaternary cationic surfactant, alkylamine oxide, dimethyl diallyl

ammonium chloride polymer, polyoxypropylene diethyl methyl ammonium chloride, and the like can be used.

Example 3

5 Plating test using a combination of a nonionic surfactant and another nonionic surfactant exhibiting cationic properties under strongly acidic conditions

 A mixture of 20 mg/l of PEG with a molecular weight of about 3,000 as a nonionic surfactant and 5 mg/l of an
10 ethylenediamine polyoxyethylene polyoxypropylene block polymer as another nonionic surfactant exhibiting cationic properties under strongly acidic conditions ($\text{pH} < 4$) was added to the above copper sulfate plating solution. As another additive, 5 mg/l of SPS was added.

15 The same plating test as in Example 1 was carried out to examine the copper filling conditions in fine trenches. As a result, excellent copper filling without voids was confirmed.

 An amphoteric surfactant such as lauryl amide propyl acetic acid betaine, lauryl aminoacetic acid betaine, or the
20 like may be used instead of the nonionic surfactant exhibiting cationic properties under strongly acidic conditions.

Comparative Example 1

Plating test using a combination of two nonionic surfactants

25 A plating solution was prepared in the same manner as in Example 1, except that PPG as a nonionic surfactant with high hydrophobicity and PEG as a nonionic surfactant with low

hydrophobicity were added to the copper sulfate plating solution in amounts to provide concentrations of 20 mg/l and 5 mg/l, respectively.

After plating, fine trenches were cut and the copper filling conditions were inspected using a microscope to confirm that there were seams and voids.

The reason for the occurrence of seams and voids is presumed to be that the highly hydrophobic PPG is adsorbed onto the bottom, in addition to the opening area, due to its high concentration of the above measured cmc and exhibits the same plating control effect on the opening area and the bottom to cause conformal deposition of plating metal.

Production of seams and voids in fine trenches were also confirmed in a plating test in which polyoxyethylene dimethylammonium chloride, a cationic surfactant, was used instead of PPG.

Reference Example 1

Selection of electric resistor

The electric resistor was selected from porous materials which can allow impregnation of the plating solution thereinto. Since the current between the electrodes flows through the plating solution filled into the hollow parts of the electric resistor, suitable selection of the electric resistor in respect of the material quality, porosity, and pore size is essential. Therefore, two types of materials, SiC and Al₂O₃, each having different porosity and pore sizes were

prepared. These materials were inserted between the electrodes in an electroplating bath filled with a plating solution. The electric current and voltage were measured during a plating operation to determine the resistance.

5 The resistance under the conditions in the absence of an electric resistor was subtracted from the measured resistance. The electric conductivity of the electric resistor was determined from the resulting difference in resistance. The relation between porosity and the electric
10 conductivity and the relation between the pore size and the electric conductivity are shown respectively in Figure 1 and Figure 2. The electric conductivity tends to increase in proportion to the porosity and as the pore size increases below a certain value. Also, there was no impact on the quality of
15 the materials.

 In view of the above results, the electric resistor having a porosity and pore size respectively within the dotted lines shown by the graphs was used. In regard to the material, SiC was selected in view of its porosity with a good pore size
20 distribution in the plane.

Example 4

 In-plane uniformity and filling performance in the case of using an electric resistor were tested using the cell
25 schematically shown in Figure 3. In the Figure, 1 indicates a plating cell, 2 indicates a wafer, 3 indicates an anode, 4 indicates an electric resistor, 5 indicates a wafer seal, and

6 indicates a cathode. A silicon wafer with a size of 200 mm x 300 mm treated with SiO₂, TaN, Ta, and Cu in that order was used. Thicknesses of 20 nm and 60 nm were used for the copper seed layer.

5 The wafer was mounted on a stage with the process plane upward. An SiC foil with a thickness of 10 mm was disposed between the anode and the wafer. A seal for preventing leakage of the plating solution and a cathode contact point were disposed on the periphery of the wafer. The plating solution
10 was introduced into the space between the electric resistor and the wafer. The composition of the plating solution and the plating conditions were as follows.

(Plating solution composition)

15	Copper sulfate pentahydrate	225 g/l
	Sulfuric acid	55 g/l
	Chlorine	60 ppm
	Additive (PEG)	22 ml/l

(Plating conditions)

20 Current: Direct current
 Current density: 20 mA/cm²
 Bath temperature: 25°C
 Plating time: 2 minutes

(Measuring method)

25 The film thickness after plating was determined by measuring the sheet resistance of the copper film using the direct-current four-probe method and converting the resistance

into the film thickness using a known resistance-thickness conversion rate. The in-plane distribution and uniformity of the film thickness were determined by measuring the thickness at 355 points within 4 mm inside the edge in the diameter direction.

(Test result)

Figure 4 shows a result of measuring a film thickness distribution in the periphery of a 200 mm wafer and Figure 5 shows a result of measuring a film thickness distribution in the periphery of a 300 mm wafer. The in-plane distribution in the case of the seed film thickness of 20 nm was almost the same as that in the case of the seed film thickness of 60 nm. No tendency of a film thickness increase in the edge portion was identified. The in-plane uniformity (3σ) obtained when plating a 300 mm substrate to produce a 1.0 μm plating film was 3% or less.

Example 5

A substrate with a thickness of 300 mm with a 60 nm copper seed layer formed thereon (pretreated in the same manner as in Example 1) was plated under the following conditions for a period of time to produce films with an average thickness of 0.5 μm , 1.0 μm , and 2.5 μm . After plating, the film thickness distribution was measured. The results are shown in Figure 6. In any of the cases of an average thickness of 0.5 μm , 1.0 μm , and 2.5 μm , the in-plane uniformity (3σ) was 2.2-3.3%, indicating that there was no significant thickness change in

the in-plane distribution.

(Plating solution composition)

	Copper sulfate pentahydrate	225 g/l
5	Sulfuric acid	55 g/l
	Chlorine	60 ppm
	Additive (PEG)	22 ml/l

(Plating conditions)

	Current: Direct current
10	Current density: 20 mA/cm ²
	Bath temperature: 25°C

The relation between the sulfuric acid concentration and electric conductivity of the copper sulfate plating solution is shown in Figure 7, which shows that conventional plating without using an electric resistor was effected at the sulfuric acid concentration in the range of 10-60 g/l and the electric conductivity in the range of 6-20 S/m. In contrast, based on the fact that plating was possible at the electric conductivity of 3 S/m or less as shown in Figures 2 and 3, it can be judged that excellent in-plane uniformity was achieved when an electric resistor was used.

Figure 8 shows the calculation result of the electric conductivity and thickness distribution (recess conditions in the center of the wafer) when the seed layer was varied by the finite element method (FEM). The result also shows the effect of the seed film thickness on the electric conductivity and film

thickness distribution.

Example 6

A barrier layer and copper seed layer (with a seed layer
5 thickness of 80nm near the vias) were formed according to a
conventional method on a semiconductor silicon substrate having
vias with an opening of 0.14 μm and an aspect ratio of 5 formed
thereon to prepare a test sample. This test sample was used
for a plating test using the acid copper plating solution 1
10 having the composition shown below and a chip testing instrument
(liquid volume: 1 l) schematically shown in Figure 9. Plating
was carried out at a current density of 3 mA/cm^2 , a plating bath
temperature of 25°C, and mechanical stirring using a stirrer
at no more than 400 rpm for 3 minutes.

15

(Composition of plating solution 1)

	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	200 g/l
	H_2SO_4	10 mol/l
	Cl^-	60 ppm
20	PEG (molecular weight: about 3,000)	1,000 ppm
	SPS	5 ppm
	Polyethylene imine	1 ppm

The section of vias after plating was inspected by a
25 scanning electron microscope (SEM) to confirm that there were
no voids produced.

Example 7

A plating test was carried out on the sample of Example 6 using the plating solution 1 of Example 6 and the following plating solution 2 in two chip testing instruments. Plating was carried out at a current density of 15 mA/cm² for 5 seconds using the plating solution 1, then at a current density of 6 mA/cm² for 3 minutes using the plating solution 2. The plating bath temperature was 25°C.

10 (Composition of plating solution 2)

	CuSO ₄ ·5H ₂ O	200 g/l
	H ₂ SO ₄	10 mol/l
	Cl ⁻	60 ppm
	PEG (molecular weight: about 3,000)	200 ppm
15	SPS	5 ppm
	Polyethylene imine	1 ppm

The section of vias after plating was inspected by SEM to confirm that there were no voids produced.

20

Comparative Example 2

A plating test was carried out in the same manner as in Example 6 using the same sample of Example 6, except that the plating solution 3 with the following composition was used.

25

(Composition of plating solution 3)

CuSO ₄ ·5H ₂ O	200 g/l
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	H ₂ SO ₄	10 mol/l
	Cl ⁻	60 ppm
	PEG (molecular weight: about 3,000)	200 ppm
	SPS	5 ppm
5	Polyethylene imine	1 ppm

The section of vias after plating was inspected by SEM to confirm that there were no voids produced.

10 INDUSTRIAL APPLICABILITY

The acid copper plating solution of the present invention can be applied to the surface of wafers or the like having submicron-level gaps to completely fill the gaps with copper plating and, at the same time, form highly uniform copper plating at a higher electrocoating speed.

According to the first plating method of the present invention, copper plating with excellent in-plane thickness uniformity can be obtained without being affected by the seed film thickness and plating thickness by using a plating bath with a specific acid concentration and inserting an electric resistor between the electrodes. In particular, because excellent filling can be ensured even in the case in which a concave-convex pattern on a semiconductor substrate contains circuit trenches or vias with a width of 0.1 μm or less, the method is expected as a useful means for achieving excellent in-plane uniformity in the copper wiring plating after the 65 nm generation.

According to the second plating method of the present invention, uniform plating can be ensured while preventing void formation, even in very small holes and trenches where the copper seed film is extremely thin without causing copper to
5 be dissolved in the plating solution.

Therefore, the present invention is extremely useful as a technology for plating the surface of wafers, which are semiconductor materials, particularly for forming circuit patterns having submicron-level trenches on electronic circuit
10 substrates such as wafers, semi-conductor substrates, or printed boards by using metal plating such as copper plating. The present invention can therefore be used with advantage for manufacturing next generation electronic circuit boards with an increasing density of wiring circuits.

15